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Publication number: **0 249 150 B1**

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## EUROPEAN PATENT SPECIFICATION

- ④⑤ Date of publication of patent specification: 29.05.91 ⑤① Int. Cl.<sup>5</sup>: **C07C 323/52**, C07C 323/22,  
C07C 331/02, C07C 323/28,  
②① Application number: 87108080.0 C07C 315/02, A01N 35/06,  
C07C 317/24, C07C 317/44  
②② Date of filing: 04.06.87

⑤④ Certain 3-(substituted thio)-2-benzoyl-cyclohex-2-enones.

③③ Priority: 09.06.86 US 872078

④③ Date of publication of application:  
16.12.87 Bulletin 87/51

④⑤ Publication of the grant of the patent:  
29.05.91 Bulletin 91/22

⑥④ Designated Contracting States:  
BE CH DE FR GB GR IT LI NL

⑤⑥ References cited:

None.

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**EP 0 249 150 B1**

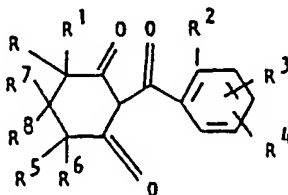
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## EP 0 249 150 B1

## Description

This invention relates to 3-(substituted thio)-2-benzoyl-cyclo-hex-2-enones and their use as herbicides.

EP-A-135 191 refers to certain 2-(2-substituted benzoyl)-1,3-cyclohexanediones having the structural formula



wherein R is C<sub>1</sub>-C<sub>6</sub> alkyl; R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl, or

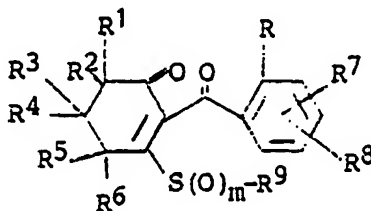


wherein R<sup>a</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or R and R<sup>1</sup> together are alkylene having 3 to 6 carbon atoms; R<sup>2</sup> is chlorine, bromine, iodine or C<sub>1</sub>-C<sub>4</sub> aliphatic alkoxy; R<sup>3</sup> and R<sup>4</sup> independently are hydrogen or an aliphatic group; R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl; and R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl; and their salts.

One embodiment of this invention is an herbicidal composition comprising an herbicidally active 3-(substituted thio)-2-benzoyl-cyclohex-2-enones and an inert carrier therefor wherein the 2-position of the benzoyl moiety is substituted as herein recited and the 4-position preferably is substituted with an electron withdrawing group, such as halogen, cyano or trifluoromethyl. The 4-, 5- and 6-positions of the cyclohex-2-enone moiety can be substituted, preferably with the groups hereinafter recited.

More preferably, the cyclohex-2-enone moiety has no substitution or the 4-or 6-position is substituted with two methyl groups. The 3-, 4- and 5-positions of the benzoyl moiety can be substituted, preferably with the groups hereinafter recited.

Also embodied within the scope of this invention are novel compounds having the following structural formula



wherein

R is halogen; C<sub>1</sub>-C<sub>2</sub> alkyl, preferably methyl; C<sub>1</sub>-C<sub>2</sub> alkoxy, preferably methoxy; nitro; cyano; C<sub>1</sub>-C<sub>2</sub> haloalkyl, preferably trifluoromethyl; or R<sup>a</sup>SO<sub>n</sub>- wherein n is 0 or 2, preferably 2 and R<sup>a</sup> is C<sub>1</sub>-C<sub>2</sub> alkyl, preferably methyl. Preferably, R is chlorine, bromine, C<sub>1</sub>-C<sub>2</sub> alkyl, C<sub>1</sub>-C<sub>2</sub> alkoxy, cyano, nitro, C<sub>1</sub>-C<sub>2</sub> alkylthio or C<sub>1</sub>-C<sub>2</sub> alkylsulfonyl; more preferably chlorine, nitro, methyl, trifluoromethyl or methylsulfonyl;

R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>1</sup> is hydrogen or methyl;

R<sup>2</sup> is hydrogen; C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>2</sup> is hydrogen or methyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 2 to 5 carbon atoms;

## EP 0 249 150 B1

$R^3$  is hydrogen or  $C_1$ - $C_4$  alkyl, preferably  $C_1$ - $C_2$  alkyl, more preferably methyl; most preferably  $R^3$  is hydrogen or methyl;

$R^4$  is hydrogen or  $C_1$ - $C_4$  alkyl, preferably  $C_1$ - $C_2$  alkyl more preferably methyl; most preferably  $R^4$  is hydrogen or methyl; or

5  $R^3$  and  $R^4$  together can be oxo;

$R^5$  is hydrogen or  $C_1$ - $C_2$  alkyl, preferably methyl, more preferably  $R^5$  is hydrogen or methyl;

$R^6$  is hydrogen or  $C_1$ - $C_2$  alkyl, preferably methyl, more preferably  $R^6$  is hydrogen; or

$R^5$  and  $R^6$  together are alkylene having 2 to 5 carbon atoms;

10  $R^7$  and  $R^8$  substituting the 3-, 4- and 5-positions of the benzoyl moiety independently are (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3)  $C_1$ - $C_4$  alkyl, preferably methyl; (4)  $C_1$ - $C_4$  alkoxy, preferably methoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8)  $C_1$ - $C_4$  haloalkyl, more preferably trifluoromethyl; (9)  $R^bSO_n$ - wherein n is the integer 0, 1 or 2, preferably 2; and

$R^b$  is

(a)  $C_1$ - $C_4$  alkyl, preferably methyl;

15 (b)  $C_1$ - $C_4$  alkyl substituted with halogen or cyano, preferably chloromethyl, trifluoromethyl or cyanomethyl;

(c) phenyl; or

(d) benzyl;

(10)  $-NR^cR^d$  wherein

20  $R^c$  and  $R^d$  independently are hydrogen or  $C_1$ - $C_4$  alkyl;

(11)  $R^eC(O)-$  wherein

$R^e$  is  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy;

(12)  $-SO_2NR^cR^d$  wherein  $R^c$  and  $R^d$  are as defined;

(13)  $-N(R^e)C(O)R^d$  wherein  $R^c$  and  $R^d$  are as defined; and

25 m is the integer 0, 1 or 2, preferably 0 or 2, most preferably 2;

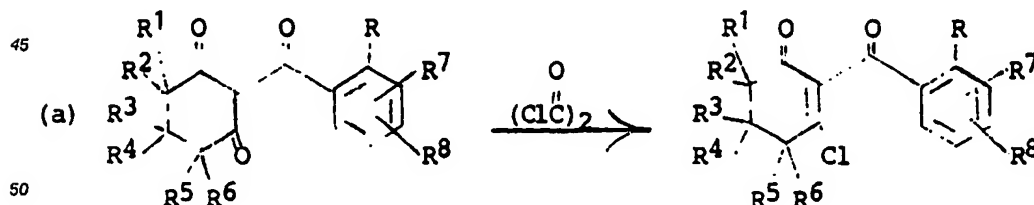
$R^9$  is  $C_1$ - $C_4$  alkyl, preferably methyl or ethyl; phenyl; substituted phenyl; cyano;  $-(CH_2)_xC(O)O-(C_1-C_4$  alkyl) wherein x is the integer 1, 2 or 3.

30 The term " $C_1$ - $C_4$  alkyl" includes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and t-butyl. The term "halogen" includes chlorine, bromine, iodine and fluorine. The term " $C_1$ - $C_4$  alkoxy" includes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy. The term " $C_1$ - $C_4$  haloalkyl" includes the alkyl groups defined above under  $C_1$ - $C_4$  alkyl in which one or more hydrogen is replaced by chloro, bromo, iodo or fluoro.

35 Preferably,  $R^7$  is in the 3-position. Most preferably  $R^7$  is hydrogen. Preferably  $R^8$  is in the 4-position. Most preferably  $R^8$  is halogen, cyano, trifluoromethyl, or  $R^bSO_2$  wherein  $R^b$  is  $C_1$ - $C_4$  alkyl, preferably methyl or  $C_1$ - $C_4$  haloalkyl, preferably chloromethyl, difluoromethyl or trifluoromethyl.

The compounds of this invention are active herbicides of a general type. That is, they are herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of the above-described compounds to the area where control is desired.

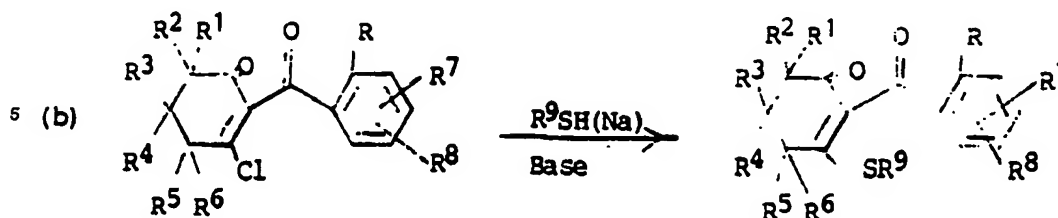
40 The compounds of the present invention can be prepared by the following two- or, if necessary, three-step general method.



wherein R through  $R^8$  are as defined.

55 Generally in step (a) the benzoyl dione is dissolved in an inert solvent such as methylene dichloride and an excess, usually 150 to 200 mole percent, of oxalyl chloride is added followed by a catalytic amount (0.1 equivalent) of dimethylformamide. The reaction mixture is stirred from one hour to one day at room temperature. The reaction product is isolated using conventional techniques.

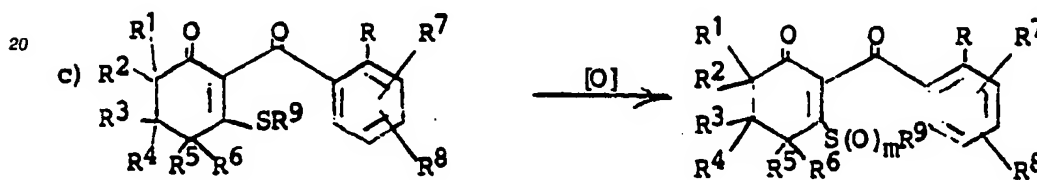
## EP 0 249 150 B1



wherein R through R<sup>9</sup> are as defined.

Generally, in step (b) the 3-chloro-2-benzoylcycloalkenone is dissolved in an inert solvent such as tetrahydrofuran and the thiol (1.0 to 2.0 equivalents) is added, followed by a base (1.0 to 2.0 equivalents) such as triethylamine and the solution is stirred 1 to 8 hours at room temperature and the product is isolated using conventional techniques.

Alternatively in step (b), the thiol can be added as a thiolate, preferably the sodium thiolate. The product in step (b) can then be isolated using standard techniques.

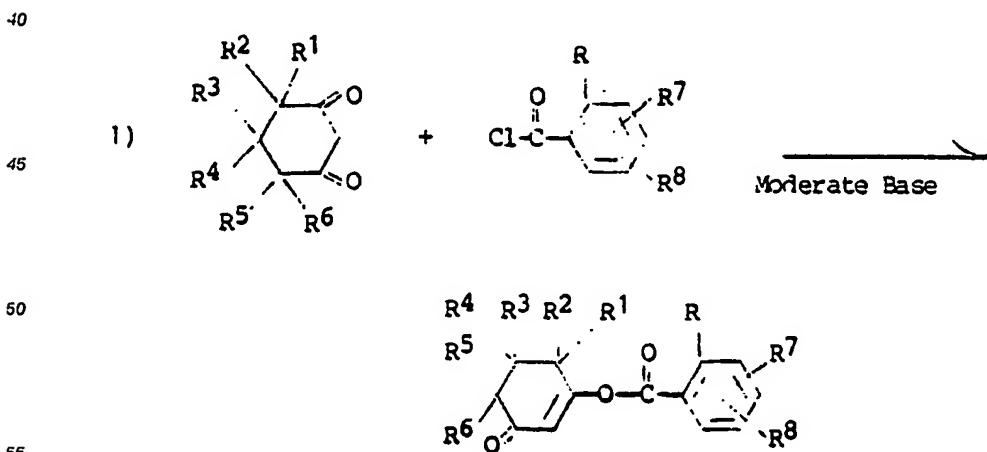


wherein R through R<sup>9</sup> are as defined, m is the integer 1 or 2 and [O] is an oxidizing agent, preferably peroxides such as peracetic acid.

Generally, in reaction step (c) the vinylsulfide is dissolved in methylene chloride and an oxidizing agent such as m-chloroperoxybenzoic acid (1.1-2.2 equivalents) is added portion-wise and the reaction stirred for 1 to 8 hours. The product may be isolated using conventional techniques.

The precursor benzoyl diones used in step (a) can be prepared by the following two-step general method.

The process proceeds via the production of an enol ester intermediate as shown in reaction (1). The final product is obtained by rearrangement of the enol ester as shown in reaction (2). The two reactions may be conducted as separate steps by isolation and recovery of the enol ester using conventional techniques prior to conducting step (2), or by addition of a cyanide source to the reaction medium after the formation of the enol ester, or in one step by inclusion of the cyanide source at the start of reaction (1).

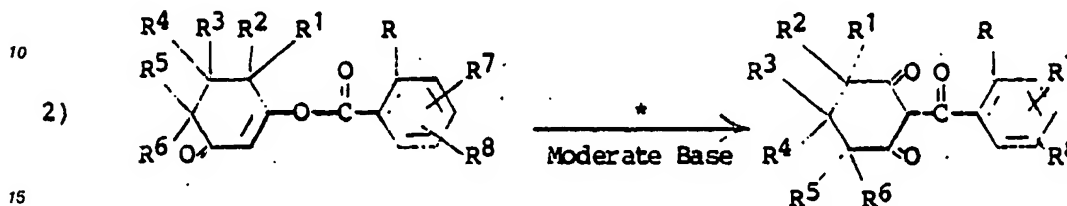


wherein R through R<sup>8</sup> are as defined and the moderate base is as defined, preferably tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, alkali metal carbonate or alkali metal phosphate.

## EP 0 249 150 B1

Generally, in step (1) mole amounts of the dione and substituted benzoyl reactant are used, along with a mole amount or excess of the base. The two reactants are combined in an organic solvent such as methylene chloride, toluene, ethyl acetate or dimethylformamide. The base or benzoyl reactant preferably is added to the reaction mixture with cooling. The mixture is stirred at 0°C-50°C until the reaction is substantially complete.

The reaction product is worked up by conventional techniques.



\* = Cyanide source.

Moderate base = as defined herein.

wherein R through R<sup>8</sup> are as defined.

Generally, in step (2) a mole of the enol ester intermediate is reacted with 1 to 4 moles of the moderate base, preferably about 2 moles of moderate base and from 0.01 mole to about 0.5 mole or higher, preferably about 0.1 mole of the cyanide source (e.g., potassium cyanide or acetone cyanohydrin). The mixture is stirred in a reaction pot until the rearrangement is substantially complete at a temperature below 80°C, preferably about 20°C to about 40°C, and the desired product is recovered by conventional techniques.

The term "cyanide source" refers to a substance or substances which under the rearrangement conditions consists of or generates hydrogen cyanide and/or cyanide anion.

The process is conducted in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C<sub>2</sub>-C<sub>5</sub> aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Hydrogen cyanide is considered most advantageous as it produces relatively rapid reaction and is inexpensive. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin.

The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. It may be used in as little as about 1 mole percent to produce an acceptable rate of reaction at about 40°C on a small scale. Larger scale reactions give more reproducible results with slightly higher catalyst levels of about 2 mole percent. Generally about 1-10 mole % of the cyanide source is preferred.

The process is conducted with a molar excess, with respect to the enol ester, of a moderate base. By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this embodiment include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine. Suitable inorganic bases include potassium carbonate and trisodium phosphate.

The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

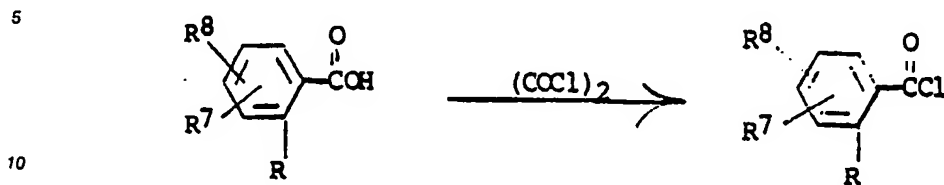
A number of different solvents are useful in this process, depending on the nature of the acid chloride or the acylated product. A preferred solvent for this reaction is 1,2-dichloroethane. Other solvents which can be employed, depending on the reactants or products include toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide, and methyl isobutyl ketone (MIBK).

In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 50°C.

The above described substituted benzoyl chlorides can be prepared from the corresponding substituted

## EP 0 249 150 B1

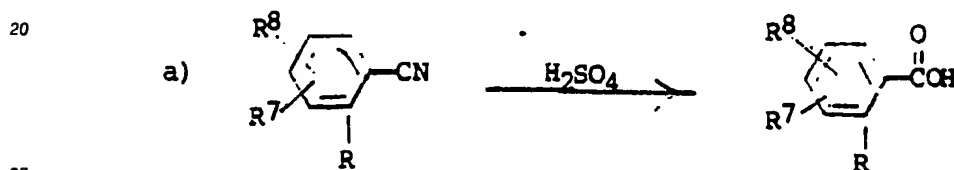
benzoic acids according to the teaching of Reagents for Organic Synthesis, Vol. I, L.F. Fieser and M. Fieser, pp. 767-769 (1967).



wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

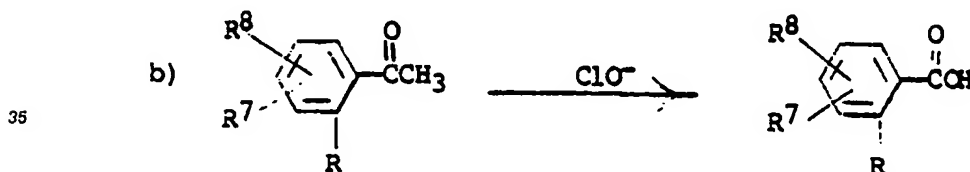
The substituted benzoic acids can be prepared by a wide variety of general methods according to the teaching of The Chemistry of Carboxylic Acids and Esters, S. Patai, editor, J. Wiley and Sons, New York, N.Y. (1969) and Survey of Organic Synthesis, C.A. Buehler and D.F. Pearson, J. Wiley and Sons, (1970).

The following are four representative examples of the methods described therein.



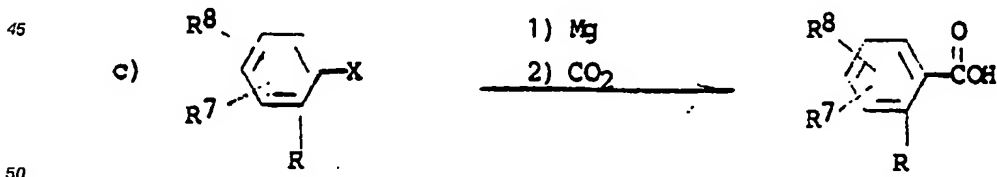
wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

In reaction (a) the substituted benzonitrile is heated to reflux in aqueous sulfuric acid for several hours. The mixture is cooled and the reaction product is isolated by conventional techniques.



wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

In reaction (b) the substituted acetophenone is heated to reflux for several hours in an aqueous hypochlorite solution. The mixture is cooled and the reaction product is isolated by conventional techniques.



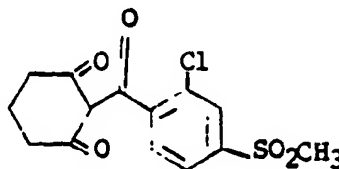
wherein R, R<sup>7</sup> and R<sup>8</sup> are as defined and X is chlorine, bromine or iodine.

The substituted aromatic halide is allowed to react with magnesium in a solvent such as ether. The solution is then poured over crushed dry ice and the benzoic acid is isolated by conventional techniques.

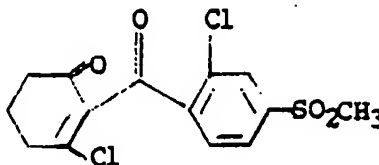
The following examples teach the synthesis of a representative compound of this invention.

# EXAMPLE I

## EP 0 249 150 B1

2-(2-Chloro-4-methanesulfonylbenzoyl)-cyclohexane-1,3-dione

1,3-Cyclohexanedione [11.2 grams (g), 0.1 mole] and 23.3 g (0.1 mole) 2-chloro-4-methanesulfonylbenzoyl chloride were dissolved in 200 ml methylene chloride at room temperature. Triethylamine (11 g, 0.11 mole) was slowly added with cooling. The reaction mixture was stirred at room temperature for 5 hours and then poured into 2N hydrochloric acid. The aqueous phase was discarded and the organic phase dried with  $\text{MgSO}_4$  and then evaporated to yield the intermediate enol ester 3-(2-chloro-4-methanesulfonylbenzoyloxy)cyclohex-2-enone. The 3-(2-chloro-4-methanesulfonylbenzoyloxy)cyclohex-2-enone was dissolved in 200 ml acetonitrile and triethylamine (22 g, 0.22 mole) was added all at once, followed by acetonecyanohydrin (0.8 g, 0.01 mole). The solution was stirred for 5 hours and then poured into 2N HCl and extracted twice with ethyl acetate. The organic layer was dried with  $\text{MgSO}_4$  and the solvent evaporated to yield the product.

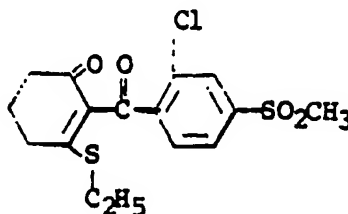
EXAMPLE II3-Chloro-2-(2-chloro-4-methanesulfonylbenzoyl)-cyclohex-2-enone

2-(2-Chloro-4-methanesulfonylbenzoyl)-cyclohexane-1,3-dione (9.8 g, 30 millimole) was dissolved in 100 ml methylene chloride and stirred at room temperature. To this solution was added oxalyl chloride (5.7 g, 45 mmol) followed by dimethylformamide (0.5 ml) in portions small enough to control effervescence. The resulting solution was stirred for 4 hours and then poured into water and extracted with methylene chloride. The organic layer was washed again with water, saturated  $\text{K}_2\text{CO}_3$  solution and then dried with  $\text{MgSO}_4$  and the solvent evaporated to yield 3-chloro-2-(2-chloro-4-methanesulfonylbenzoyl)cyclohex-2-enone (7.3 g, 70%) as an oil which was used without further purification.

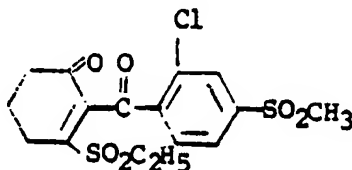
EXAMPLE III3-Thioethyl-2-(2-chloro-4-methanesulfonylbenzoyl)-cyclohex-2-enone



## EP 0 249 150 B1



3-Chloro-2-(2-chloro-4-methanesulfonylbenzoyl)cyclohex-2-enone (4.2 g, 12 mmol) was dissolved in 80 ml THF and ethane thiol (0.75 g, 12 mmol) and triethylamine (1.2 g, 12 mmol) were added and the solution stirred for 18 hours. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with 1N HCl, 1N NaOH, water, dried with  $\text{MgSO}_4$  and then evaporated to yield 2.9 g (65%) of a rust colored solid, m.p. 151-154 °C.

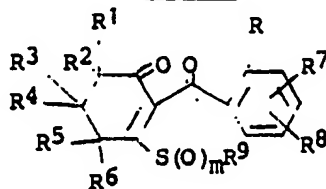
EXAMPLE IV3-Ethanesulfonyl-2-(2-chloro-4-methanesulfonylbenzoyl)cyclohex-2-enone

3-Thioethyl-2-(2-chloro-4-methanesulfonylbenzoyl)-cyclohex-2-enone (2.0 g, 5.4 mmol) was dissolved in 50 ml methylene chloride and cooled to 0 °C. m-Chloroperoxybenzoic acid (2.2 g, 10 mmol @ 80%) was added portion-wise and then stirred for several hours. When TLC showed the reaction was complete, the reaction mixture was transferred to a separatory funnel, more  $\text{CH}_2\text{Cl}_2$  was added and the mixture shaken with  $\text{Na}_2\text{S}_2\text{O}_5$  solution, and then 5%  $\text{K}_2\text{CO}_3$ . The organic layer was dried with  $\text{MgSO}_4$  and the solvent evaporated to afford 1.1 g of solid, m.p. 157-161 °C.

The following is a table of certain selected compounds that are preparable according to the procedure described herein. Compound numbers are assigned to each compound and are used throughout the remainder of the application.

## EP 0 249 150 B1

TABLE I



Cmpd.												m.p.
No.	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	m	R <sup>9</sup>	°C
15	1	Cl	H	H	H	H	H	3-Cl	4-Cl	0	C <sub>2</sub> H <sub>5</sub> OC(O)CH <sub>2</sub> -	55-58
	2	Cl	H	H	H	H	H	3-Cl	4-Cl	0	phenyl	oil
	3	Cl	H	H	H	H	H	H	4-Cl	0	CH <sub>3</sub>	oil
	4	Cl	H	H	H	H	H	H	4-Cl	2	CH <sub>3</sub>	oil
20	5	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	2	C <sub>2</sub> H <sub>5</sub>	142-147
	6a)	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	2	C <sub>2</sub> H <sub>5</sub>	157-161
	7	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	2	CH <sub>3</sub>	81-86
	8	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	0	CH <sub>3</sub> OC(O)CH <sub>2</sub> -	
25	9	Cl	H	H	H	H	H	H	4-Cl	0	CH <sub>3</sub> OC(O)CH <sub>2</sub> -	oil
	10	Cl	H	H	H	H	H	3-Cl	4-Cl	0	CH <sub>3</sub> OC(O)CH <sub>2</sub> -	oil
	11	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	CH <sub>3</sub> OC(O)CH <sub>2</sub> -	oil
	12	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	2	CH <sub>3</sub>	
30	13	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	2	CH <sub>3</sub> OC(O)CH <sub>2</sub> -	119-124
	14	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	CN	123-126
	15	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	0	2, 3-dichlorophenyl	121-125
	16	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	4-methoxyphenyl	oil
35	17	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	phenyl	186-188
	18	Cl	H	H	H	H	H	H	4-Cl	0	phenyl	oil
	19	Cl	H	H	H	H	H	H	4-Cl	2	phenyl	oil
	20	Cl	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	3-methylphenyl	oil
40	21	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	0	phenyl	152-156

## EP 0 249 150 B1

TABLE I  
(continued)

5	Compd.										m.p.		
	No.	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	m	R <sup>9</sup>	°C
	22	Cl	H	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	0	2,3-dichlorophenyl	165-169
	23	Cl	H	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	2	3-methylphenyl	oil
10	24	Cl	H	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	2	4-methoxyphenyl	99-109
	25	Cl	H	H	H	H	H	H	H	4-Cl	0	3-methylphenyl	oil
	26	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	2	2,3-dichlorophenyl	75-76
	27	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	2	phenyl	oil
15	28	Cl	H	H	H	H	H	H	3-OC <sub>2</sub> H <sub>5</sub>	4-SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0	CH <sub>3</sub>	oil
	29	Cl	H	H	H	H	H	H	H	4-SO <sub>2</sub> CH <sub>3</sub>	1	2,3-dichlorophenyl	97-102
	30	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	1	3-methylphenyl	oil
20	31	Cl	H	H	H	H	H	H	H	4-Cl	2	2,3-dichlorophenyl	161-164
	32	Cl	H	H	H	H	H	H	3-Cl	4-Cl	0	3-methylphenyl	oil
	33	Cl	H	H	H	H	H	H	3-Cl	4-Cl	0	phenyl	oil
	34	Cl	H	H	H	H	H	H	H	4-Cl	0	4-methoxyphenyl	oil
25	35	Cl	H	H	H	H	H	H	H	4-Cl	2	4-methoxyphenyl	oil
	36	Cl	H	H	H	H	H	H	3-Cl	4-Cl	2	phenyl	69-74
	37	Cl	H	H	H	H	H	H	3-C <sub>2</sub> H <sub>5</sub> O	4-SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	2	CH <sub>3</sub>	60-63

a) = Prepared in Example IV.

## Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Selected compounds of this invention were tested as herbicides in the following manner.

Pre-emergence herbicide test. On the day preceding treatment, seeds of seven different weed species are planted in loamy sand soil in individual rows using one species per row across the width of a flat. The weeds used are green foxtail (FT) (*Setaria viridis*), watergrass (WG) (*Echinochloa crusgalli*), wild oat (WO) (*Avena fatua*), annual morningglory (AMG) (*Ipomoea lacunosa*), velvetleaf (VL) (*Abutilon theophrasti*), Indian mustard (MD) (*Brassica juncea*) and yellow nutsedge (YNS) (*Cyperus esculentus*). Ample seeds are planted to give about 20 to 40 seedlings per row, after emergence, depending upon the size of the plants.

Using an analytical balance, 600 milligrams (mg) of the compound to be tested are weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 60 milliliter (ml) wide-mouth clear bottle and dissolved in 45 ml of acetone or substituted solvent. Eighteen ml of this solution are transferred to a 60 ml wide-mouth clear bottle and diluted with 22 ml of a water and acetone mixture (19:1) containing enough polyoxyethylene sorbitan monolaurate emulsifier to give a final solution of 0.5% (v/v). The solution is then sprayed on a seeded flat on a linear spray table calibrated to deliver 748 L/ha (80 gallons per acre). The application rate is 4.48 kg/ha (4 lb/acre).

After treatment, the flats are placed in the greenhouse at a temperature of 21 to 27 °C (70 to 80 °F) and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as percent control with 0% representing no injury and 100% representing complete control.

The results of the tests are shown in the following Table II.

## EP 0 249 150 B1

TABLE II

Pre-Emergence Herbicidal Activity  
Application Rate -- 4.48 kg/ha

5	Cmpd. No.	FT	WG	WO	AMG	VL	MD	YNS
	1	0	0	0	0	0	0	0
	2	15	45	0	0	50	30	0
10	3	60	40	0	0	50	50	40
	4	98	100	0	40	100	100	80
	5	100	85	100	20	100	100	80
	6	100	100	90	100	100	100	80
15	7	100	100	90	95	100	100	80
	8	100	100	70	30	100	90	70
	9	0	10	0	5	100	100	10
	10	0	10	0	0	100	100	70
20	11	0	0	0	0	0	0	0
	12	100	100	70	10	100	95	80
	13	98	98	50	90	100	80	70
	14	50	100	0	25	100	100	80
	15	0	0	10	0	0	0	0
25	16	0	10	80	95	100	80	80
	17	10	5	90	100	95	80	80
	18	0	0	0	0	0	0	0
	19	80	5	90	100	100	50	80
30	20	0	0	80	50	90	10	80
	21	0	0	0	0	0	0	0
	22	0	0	0	0	0	0	0
35	23	100	30	100	100	100	40	80
	24	85	10	100	100	90	50	80
	25	0	0	20	20	0	0	10
	26	100	95	100	95	100	30	80
	27	100	95	100	90	100	10	80
40	28	100	80	100	100	100	90	80
	29	100	80	100	100	100	80	80
	30	100	100	100	100	100	20	80
	31	0	0	10	10	0	0	30
45	32	50	0	10	10	0	0	0
	33	0	0	10	0	0	0	0
	34	50	0	80	100	100	0	80
	35	0	0	70	100	100	5	80
50	36	0	0	30	100	90	5	0
	37	100	100	100	100	100	100	80

Post-Emergence Herbicide Test: This test is conducted in an identical manner to the testing procedure for the pre-emergence herbicide test, except the seeds of the seven different weed species are planted 10-12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence herbicide test are reported in Table III.

## EP 0 249 150 B1

TABLE III

Post-Emergence Herbicidal Activity  
Application Rate -- 4.48 kg/ha

5	Cmpd. No.	FT	WG	WO	AMG	VL	MD	YNS
	1	40	60	10	15	60	60	50
10	2	10	50	0	30	90	100	0
	3	60	40	0	0	50	50	40
	4	0	40	0	40	80	50	5
	5	75	70	70	60	60	40	80
	6	100	100	95	100	100	100	80
15	7	90	85	95	80	95	95	60
	8	98	80	80	60	80	75	70
	9	90	100	90	80	100	85	10
	10	85	95	0	70	100	90	10
20	11	0	0	0	0	0	0	0
	12	90	60	50	40	80	60	80
	13	90	80	80	40	100	90	70
	14	10	50	10	40	80	70	10
	15	80	20	80	20	90	20	5
25	16	90	80	100	90	100	100	80
	17	30	30	100	90	100	100	60
	18	10	0	90	80	100	100	5
	19	70	5	100	100	100	100	80
30	20	5	10	95	100	100	100	70
	21	0	20	60	20	80	20	0
	22	10	20	70	50	50	20	0
35	23	95	85	90	100	100	85	80
	24	100	80	100	100	100	100	80
	25	10	0	90	100	100	75	30
	26	90	80	80	80	90	75	80
40	27	90	80	85	80	100	50	80
	28	100	70	100	90	90	90	80
	29	100	90	95	100	100	90	80
	30	100	90	90	100	100	80	80
	31	0	0	80	100	100	50	70
45	32	0	0	20	80	100	50	10
	33	0	0	50	100	100	40	5
	34	10	0	85	100	100	100	30
	35	0	0	70	100	90	20	30
50	36	0	0	30	80	80	50	10
	37	80	50	50	80	70	20	80

The compounds of the present invention are useful as herbicides and can be applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the materials in a given

## EP 0 249 150 B1

application. Thus, these active herbicidal compounds may be formulated as granules of relatively large particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as flowables, as solutions or as any of several other known types of formulations, depending upon the desired mode of application. These formulations may contain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. A herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from  $9 \times 10^{-7}$  (0.01) to  $9 \times 10^{-4}$  kg/m<sup>2</sup> (10 pounds per acre), preferably from  $2 \times 10^{-6}$  (0.02) to  $4 \times 10^{-4}$  kg/m<sup>2</sup> (4 pounds per acre).

Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersants. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally are prepared to contain about 5% to about 95% of the active ingredient and usually also contain a small amount of wetting, dispersing, or emulsifying agent to facilitate wetting and dispersion.

Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthal, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in comprises about 0.5% to 95% of active ingredient by weight of the herbicidal composition.

Granular formulations wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, attapulgite clay, bentonite clays, montmorillonite clay, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5% to about 25% of active ingredients which may include surface-active agents such heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as destrins, glue or synthetic resins.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their salts; polyhydric alcohols; polyethoxylated alcohols; esters and fatty amines; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 15% by weight of the herbicidal composition.

Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating application.

Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5% to about 95% of active ingredient by weight, and may also contain small amounts of a wetting, dispersing or emulsifying agent to facilitate dispersion. For application, the pastes are normally diluted and applied as a spray to the area to be affected.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene and other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons, may also be used.

The phytotoxic compositions of this invention can be applied to the plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of power-dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray or by rope wick applications because they are effective in very low dosages. In order to modify or control growth of germinating seeds or emerging seedlings, as a typical example, the dust and liquid compositions can be applied to the soil according to conventional methods and can be distributed in the soil to a depth of at least 1/2 inch below the soil surface. It is not necessary that the phytotoxic compositions be mechanically admixed with the soil particles since these compositions can also be applied merely by spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

## EP 0 249 150 B1

EMULSIFIABLE CONCENTRATE FORMULATIONS

<u>General Formula with Ranges</u>		<u>Specific Formula</u>		
5	Herbicidal compound	5-55	herbicidal compound	24
	surfactant(s)	5-25	proprietary blend of oil-	10
	solvent(s)	20-90	soluble sulfonates and	
		<u>100%</u>	polyoxyethylene ethers	
10			polar solvent	27
			petroleum hydrocarbon	39
				<u>100%</u>

WETTABLE POWDER FORMULATIONS

15	herbicidal compound	3-90	herbicidal compound	80
	wetting agent	0.5-2	sodium dialkyl naphthalene	0.5
	dispersing agent	1-8	sulfonate	
20	diluent(s)	8.5-87	sodium lignosulfonate	7
		100%	attapulgite clay	12.5
				100%

EXTRUDED GRANULAR FORMULATIONS

25	herbicidal compound	1-20	herbicidal compound	10
	binding agent	0-10	lignin sulfonate	5
	diluent(s)	70-99	calcium carbonate	85
		100%		100%

FLOWABLE FORMULATIONS

	herbicidal compound	20-70	herbicidal compound	45
	surfactant(s)	1-10	polyoxyethylene ether	5
35	suspending agent(s)	0.05-1	attagel	0.05
	antifreeze agent	1-10	propylene glycol	10
	antimicrobial agent	1-10	1,2-benzisothiazoline-3-one	0.03
	antifoam agent	0.1-1	silicone defoamer	0.02
40	solvent	7.95-77.85	water	39.9
		100%		100%

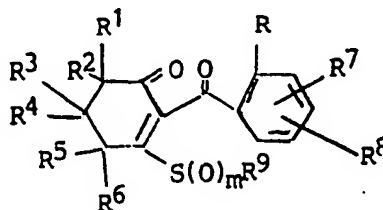
The phytotoxic compositions of this invention can also contain other additives, for example, fertilizers, other herbicides and other pesticides, used as adjuvant or in combination with any of the above-described adjuvants. Fertilizers useful in combination with the active ingredients include, for example, ammonium nitrate, urea and superphosphate.

## 50 Claims

1. A compound of the formula

55

## EP 0 249 150 B1



wherein

R is halogen, C<sub>1</sub>-C<sub>2</sub> alkyl, C<sub>1</sub>-C<sub>2</sub> alkoxy, nitro; cyano; C<sub>1</sub>-C<sub>2</sub> haloalkyl, or R<sup>a</sup>SO<sub>n</sub>- wherein n is 0 or 2 and R<sup>a</sup> is C<sub>1</sub>-C<sub>2</sub> alkyl;

R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>2</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 2 to 5 carbon atoms;

R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>4</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; or

R<sup>3</sup> and R<sup>4</sup> together can be oxo;

R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl;

R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl; or

R<sup>5</sup> and R<sup>6</sup> together are alkylene having 2 to 5 carbon atoms;

R<sup>7</sup> and R<sup>8</sup> substituting the 3-, 4- and 5-positions of the benzoyl moiety independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined; or (13) -N(R<sup>e</sup>)C(O)R<sup>d</sup> wherein R<sup>e</sup> and R<sup>d</sup> are as defined;

m is the integer 0, 1 or 2; and

R<sup>9</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; phenyl, substituted phenyl; cyano; -(CH<sub>2</sub>)<sub>x</sub>C(O)O-(C<sub>1</sub>-C<sub>4</sub> alkyl) wherein X is the integer 1, 2, or 3.

2. The compounds of Claim 1 wherein R is chlorine, bromine, C<sub>1</sub>-C<sub>2</sub> alkyl, C<sub>1</sub>-C<sub>2</sub> alkoxy, cyano, nitro, C<sub>1</sub>-C<sub>2</sub> alkylthio or C<sub>1</sub>-C<sub>2</sub> alkyl sulfonyl; R<sup>1</sup> is hydrogen or methyl; R<sup>2</sup> is hydrogen or methyl; R<sup>3</sup> is hydrogen or methyl; R<sup>4</sup> is hydrogen or methyl; R<sup>5</sup> is hydrogen or methyl; R<sup>6</sup> is hydrogen or methyl; R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined; or (13) -N(R<sup>e</sup>)C(O)R<sup>d</sup> wherein R<sup>e</sup> and R<sup>d</sup> are as defined; m is the integer 0, 1 or 2; and R<sup>9</sup> is methyl, ethyl, phenyl, CH<sub>3</sub>OC(O)CH<sub>2</sub>-, C<sub>2</sub>H<sub>5</sub>OC(O)CH<sub>2</sub>-, dichlorophenyl, methylphenyl, methoxyphenyl or cyano.

3. The compounds of Claim 2 wherein R<sup>7</sup> and R<sup>8</sup> are independently are hydrogen; chlorine; fluorine; bromine; methyl; methoxy; trifluoromethoxy; cyano; nitro; trifluoromethyl; R<sub>5</sub>SO<sub>n</sub>- wherein n is the integer 2 and R<sup>b</sup> is methyl, chloromethyl, trifluoromethyl, cyanomethyl, ethyl, or n-propyl; -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>e</sup>C(O)- where R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy or SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined and R<sup>7</sup> is in the 3-position, and R<sup>8</sup> is in the 4-position.

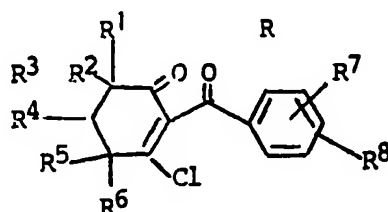
4. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidally effective amount of a compound described in Claims 1, 2 or 3.

5. An herbicidal composition comprising an herbicidally active compound of the formula 3-(substituted thio)-2-benzoyl-cyclohex-2-enones according to Claims 1, 2 or 3 and an inert carrier therefor.

6. An Intermediate compound having the structural formula



## EP 0 249 150 B1



wherein

R is halogen, C<sub>1</sub>-C<sub>2</sub> alkyl, C<sub>1</sub>-C<sub>2</sub> alkoxy, nitro; cyano; C<sub>1</sub>-C<sub>2</sub> haloalkyl, or R<sup>a</sup>SO<sub>n</sub>- wherein n is 0 or 2 and R<sup>a</sup> is C<sub>1</sub>-C<sub>2</sub> alkyl;

R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>2</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 2 to 5 carbon atoms;

R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>4</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; or

R<sup>3</sup> and R<sup>4</sup> together can be oxo;

R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl;

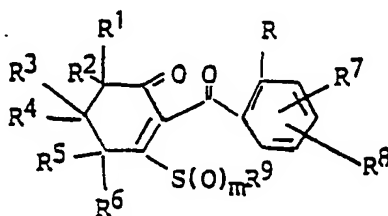
R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl; or

R<sup>5</sup> and R<sup>6</sup> together are alkylene having 2 to 5 carbon atoms;

R<sup>7</sup> and R<sup>8</sup> substituting the 3-, 4- and 5-positions of the benzoyl moiety independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined; or (13) -N(R<sup>e</sup>)C(O)R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined.

## Revendications

1. Un composé de formule :



dans laquelle

R est un atome d'halogène un groupe alkyle en C<sub>1</sub>-<sub>2</sub>; alkoxy en C<sub>1</sub>-<sub>2</sub>; nitro; cyano; haloalkyle en C<sub>1</sub>-<sub>2</sub>; ou R<sup>a</sup>SO<sub>n</sub> où n est 0 ou 2, et R<sup>a</sup> est un groupe alkyle en C<sub>1</sub>-<sub>2</sub>;

R<sup>1</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>4</sub>;

R<sup>2</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>4</sub>; ou

R<sup>1</sup> et R<sup>2</sup> forment ensemble un radical alkylène ayant 2 à 5 atomes de carbone;

R<sup>3</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>4</sub>;

R<sup>4</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>4</sub>; ou

R<sup>3</sup> et R<sup>4</sup> peuvent former ensemble un groupe oxo;

R<sup>5</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>2</sub>;

R<sup>6</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub>-<sub>2</sub>; ou

R<sup>5</sup> et R<sup>6</sup> forment ensemble un radical alkylène ayant 2 à 5 atomes de carbone;

R<sup>7</sup> et R<sup>8</sup> substituant les positions 3, 4 et 5 de la partie benzoyle sont indépendamment: (1) un

## EP 0 249 150 B1

atome d'hydrogène; (2) un atome d'halogène; (3) un groupe alkyle en C<sub>1-4</sub>; (4) un groupe alcoxy en C<sub>1-4</sub>; (5) un groupe trifluorométhoxy; (6) un groupe cyano; (7) un groupe nitro; (8) un groupe haloalkyle en C<sub>1-4</sub>; (9) R<sup>b</sup>SO<sub>n</sub>- dans lequel n est l'entier 0, 1 ou 2; et R<sup>b</sup> est (a) un groupe alkyle en C<sub>1-4</sub>; (b) un groupe alkyle en C<sub>1-4</sub> substitué par un atome d'halogène ou un groupe cyano; (c) un groupe phényle; ou (d) un groupe benzyle; (10) un groupe -NR<sup>c</sup>R<sup>d</sup> où R<sup>c</sup> et R<sup>d</sup> sont indépendamment un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; (11) un groupe R<sup>e</sup>C(O)- dans lequel R<sup>e</sup> est un groupe alkyle en C<sub>1-4</sub> ou alcoxy en C<sub>1-4</sub>; (12) un groupe -SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis; ou (13) un groupe -N(R<sup>c</sup>)C(O)R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis; et m est l'entier 0, 1 ou 2; et R<sup>3</sup> est un groupe alkyle en C<sub>1-4</sub>; un groupe phényle; un groupe phényle substitué; un groupe cyano; -(CH<sub>2</sub>)<sub>x</sub>C(O)O-alkyle en C<sub>1-4</sub> où x est l'entier 1, 2 ou 3.

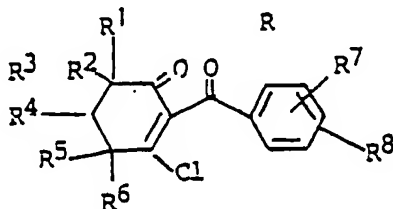
2. Les composés suivant la revendication 1, dans laquelle R est un atome de chlore, brome, un groupe alkyle en C<sub>1-2</sub>, alcoxy en C<sub>1-2</sub>, cyano, nitro, alkylthio en C<sub>1-2</sub> ou alkylsulfonyl en C<sub>1-2</sub>; R<sup>1</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>2</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>3</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>4</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>5</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>6</sup> est un atome d'hydrogène ou un groupe méthyle; R<sup>7</sup> et R<sup>8</sup> sont indépendamment: (1) un atome d'hydrogène; (2) un atome d'halogène; (3) un groupe alkyle en C<sub>1-4</sub>; (4) un groupe alcoxy en C<sub>1-4</sub>; (5) un groupe trifluorométhoxy; (6) un groupe cyano; (7) un groupe nitro; (8) un groupe haloalkyle en C<sub>1-4</sub>; (9) R<sup>b</sup>SO<sub>n</sub>- dans lequel n est l'entier 0, 1 ou 2; et R<sup>b</sup> est (a) un groupe alkyle en C<sub>1-4</sub>; (b) un groupe alkyle en C<sub>1-4</sub> substitué par un atome d'halogène ou un groupe cyano; (c) un groupe phényle; ou (d) un groupe benzyle; (10) un groupe -NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont indépendamment un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; (11) un groupe R<sup>e</sup>C(O)- dans lequel R<sup>e</sup> est un groupe alkyle en C<sub>1-4</sub> ou alcoxy en C<sub>1-4</sub>; (12) un groupe -SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis; (13) un groupe N(R<sup>c</sup>)C(O)R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis; m est l'entier 0, 1 ou 2; et R<sup>3</sup> est un groupe méthyle, éthyle, phényle, CH<sub>3</sub>OC(O)CH<sub>2</sub>-, C<sub>2</sub>H<sub>5</sub>OC(O)CH<sub>2</sub>-, dichlorophényle, méthylphényle, méthoxphényle ou cyano.

3. Les composés suivant la revendication 2, dans laquelle R<sup>7</sup> et R<sup>8</sup> sont indépendamment un atome d'hydrogène; un atome de chlore, fluor ou brome; un groupe méthyle; un groupe methoxy; un groupe trifluorométhoxy; un groupe cyano; un groupe nitro; un groupe trifluorométhyle; un groupe R<sup>b</sup>SO<sub>n</sub>- où n est égal à 2; et R<sup>b</sup> est un groupe méthyle, chlorométhyle, trifluorométhyle, cyanométhyle, éthyle ou n-propyle; un groupe -NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont indépendamment un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; un groupe R<sup>e</sup>C(O)- dans lequel R<sup>e</sup> est un groupe alkyle en C<sub>1-4</sub> ou alcoxy en C<sub>1-4</sub>; ou un groupe -SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis et R<sup>7</sup> est en position 3, et R<sup>8</sup> est en position 4.

4. Un procédé pour contrôler une végétation indésirable comprenant l'application à la zone dans laquelle un contrôle est désiré, d'une quantité efficace du point de vue herbicide d'un composé suivant les revendications 1, 2 ou 3.

5. Une composition herbicide, comprenant un composé efficace du point de vue herbicide ayant la formule 3-(thio substitué)-2-benzoylcyclohex-2-ène suivant les revendications 1, 2 ou 3 et un support inerte pour celui-ci.

6. Un composé intermédiaire ayant la formule structurale:



dans laquelle

## EP 0 249 150 B1

R est un atome d'halogène, un groupe alkyle en C<sub>1-2</sub>; alcoxy en C<sub>1-2</sub>; nitro; cyano; haloalkyle en C<sub>1-2</sub>; ou R<sup>a</sup>SO<sub>n</sub>-, où n est 0 ou 2, et R<sup>a</sup> est un groupe alkyle en C<sub>1-2</sub>;

R<sup>1</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>;

R<sup>2</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; ou

5 R<sup>1</sup> et R<sup>2</sup> forment ensemble un radical alkylène ayant 2 à 5 atomes de carbone;

R<sup>3</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>;

R<sup>4</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; ou

R<sup>3</sup> et R<sup>4</sup> peuvent former ensemble un groupe oxo;

R<sup>5</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-2</sub>;

10 R<sup>6</sup> est un atome d'hydrogène ou un groupe alkyle en C<sub>1-2</sub>; ou

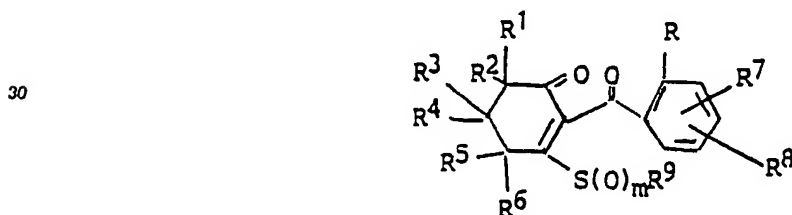
R<sup>5</sup> et R<sup>6</sup> forment ensemble un radical alkylène ayant 2 à 5 atomes de carbone;

R<sup>7</sup> et R<sup>8</sup> substituant les positions 3, 4 et 5 de la partie benzoyle sont indépendamment: (1) un atome d'hydrogène; (2) un atome d'halogène; (3) un groupe alkyle en C<sub>1-4</sub>; (4) un groupe alcoxy en C<sub>1-4</sub>; (5) un groupe trifluorométhoxy; (6) un groupe cyano; (7) un groupe nitro; (8) un groupe haloalkyle en C<sub>1-4</sub>; (9) R<sup>b</sup>SO<sub>n</sub>-, dans lequel n est l'entier 0, 1 ou 2; et R<sup>b</sup> est (a) un groupe alkyle en C<sub>1-4</sub>; (b) un groupe alkyle en C<sub>1-4</sub> substitué par un atome d'halogène ou un groupe cyano; (c) un groupe phényle; ou (d) un groupe benyle; (10) un groupe -NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont indépendamment un atome d'hydrogène ou un groupe alkyle en C<sub>1-4</sub>; (11) un groupe R<sup>e</sup>C(O)- dans lequel R<sup>e</sup> est un groupe alkyle en C<sub>1-4</sub> ou alcoxy en C<sub>1-4</sub>; (12) un groupe -SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis; ou

20 (13) un groupe -N(R<sup>c</sup>)C(O)R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis.

## Ansprüche

## 25 1. Verbindung der Formel



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R Halogen, C<sub>1</sub>-C<sub>2</sub>-Alkyl, C<sub>1</sub>-C<sub>2</sub>-Alkoxy, Nitro; Cyano; C<sub>1</sub>-C<sub>2</sub>-Haloalkyl oder R<sup>a</sup>SO<sub>n</sub>-, bedeutet, worin n für 0 oder 2 steht und R<sup>a</sup> für C<sub>1</sub>-C<sub>2</sub>-Alkyl steht;

40 R<sup>1</sup> Wasserstoff oder C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;

R<sup>2</sup> Wasserstoff oder C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet; oder

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R<sup>1</sup> oder R<sup>2</sup> zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen bedeuten;

R<sup>3</sup> Wasserstoff oder C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;

45 R<sup>4</sup> Wasserstoff oder C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet; oder

worin

R<sup>3</sup> und R<sup>4</sup> zusammen Oxo bedeuten;

R<sup>5</sup> Wasserstoff oder C<sub>1</sub>-C<sub>2</sub>-Alkyl bedeutet;

R<sup>6</sup> Wasserstoff oder C<sub>1</sub>-C<sub>2</sub>-Alkyl bedeutet; oder

50 worin

R<sup>5</sup> und R<sup>6</sup> zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen bedeuten;

R<sup>7</sup> und R<sup>8</sup>, die als Substituenten in den 3-, 4- und 5-Stellungen des Benzoyl-Molekülteils vorhanden sind, unabhängig voneinander (1) Wasserstoff; (2) Halogen; (3) C<sub>1</sub>-C<sub>4</sub>-Alkyl; (4) C<sub>1</sub>-C<sub>4</sub>-Alkoxy; (5) Trifluormethoxy; (6) Cyano; (7) Nitro; (8) C<sub>1</sub>-C<sub>4</sub>-Haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>-, worin n für die ganze Zahl 0, 1 oder 2 steht; und R<sup>b</sup> (a) für C<sub>1</sub>-C<sub>4</sub>-Alkyl; (b) für C<sub>1</sub>-C<sub>4</sub>-Alkyl, substituiert mit Halogen oder Cyano; (c) für Phenyl; oder (d) für Benzyl steht; (10) -NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> unabhängig für Wasserstoff oder C<sub>1</sub>-C<sub>4</sub>-Alkyl stehen; (11) R<sup>e</sup>C(O)-, worin R<sup>e</sup> für C<sub>1</sub>-C<sub>4</sub>-Alkyl oder C<sub>1</sub>-C<sub>4</sub>-Alkoxy steht; (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> die gegebenen Definitionen besitzen; oder (13) -N(R<sup>c</sup>)C(O)R<sup>d</sup>, worin

## EP 0 249 150 B1

$R^c$  und  $R^d$  die gegebenen Definitionen besitzen, bedeuten;

m eine ganze Zahl von 0, 1 oder 2 bedeutet; und

$R^8$   $C_1$ - $C_4$ -Alkyl; Phenyl, substituiertes Phenyl; Cyano;  $-(CH_2)_x C(O)O-(C_1-C_4\text{-Alkyl})$ , worin x für die ganze Zahl 1, 2 oder 3 steht, bedeutet.

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2. Verbindungen nach Anspruch 1, dadurch gekennzeichnet, daß R Chlor, Brom,  $C_1$ - $C_2$ -Alkyl,  $C_1$ - $C_2$ -Alkoxy, Cyano, Nitro,  $C_1$ - $C_2$ -Alkylthio oder  $C_1$ - $C_2$ -Alkylsulfonyl bedeutet;  $R^1$  Wasserstoff oder Methyl bedeutet;  $R^2$  Wasserstoff oder Methyl bedeutet;  $R^3$  Wasserstoff oder Methyl bedeutet;  $R^4$  Wasserstoff oder Methyl bedeutet;  $R^5$  Wasserstoff oder Methyl bedeutet;  $R^6$  Wasserstoff oder Methyl bedeutet;  $R^7$  und  $R^8$  unabhängig (1) Wasserstoff; (2) Halogen; (3)  $C_1$ - $C_4$ -Alkyl; (4)  $C_1$ - $C_4$ -Alkoxy; (5) Trifluormethoxy; (6) Cyano; (7) Nitro; (8)  $C_1$ - $C_4$ -Haloalkyl; (9)  $R^b SO_n$ , worin n für die ganze Zahl 0, 1 oder 2 steht; und  $R^b$  (a) für  $C_1$ - $C_4$ -Alkyl; (b) für  $C_1$ - $C_4$ -Alkyl, substituiert mit Halogen oder Cyano; (c) für Phenyl; oder (d) für Benzyl steht; (10)  $-NR^c R^d$ , worin  $R^c$  und  $R^d$  unabhängig für Wasserstoff oder  $C_1$ - $C_4$ -Alkyl stehen; (11)  $R^e C(O)-$ , worin  $R^e$  für  $C_1$ - $C_4$ -Alkyl oder  $C_1$ - $C_4$ -Alkoxy steht; (12)  $SO_2 NR^c R^d$ , worin  $R^c$  und  $R^d$  die gegebenen Definitionen besitzen; oder (13)  $-N(R^g)C(O)R^d$ , worin  $R^c$  und  $R^d$  die gegebenen Definitionen besitzen, m für eine ganze Zahl 0, 1 oder 2 steht, bedeuten; und  $R^9$  Methyl, Ethyl, Phenyl,  $CH_3 OC(O)CH_2-$ ,  $C_2H_5 OC(O)CH_2-$ , Dichlorphenyl, Methylphenyl, Methoxyphenyl oder Cyano bedeutet.

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3. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß  $R^7$  und  $R^8$  unabhängig voneinander Wasserstoff; Chlor; Fluor; Brom; Methyl; Methoxy; Trifluormethoxy; Cyano; Nitro; Trifluormethyl;  $R^b SO_n$ , worin n für die ganze Zahl 2 steht; und  $R^b$  für Methyl, Chlormethyl, Trifluormethyl, Cyanomethyl, Ethyl oder n-Propyl steht;  $-NR^c R^d$ , worin  $R^c$  und  $R^d$  unabhängig für Wasserstoff oder  $C_1$ - $C_4$ -Alkyl stehen;  $R^e-(C)O-$ , worin  $R^e$  für  $C_1$ - $C_4$ -Alkyl oder  $C_1$ - $C_4$ -Alkoxy steht; oder  $SO_2 NR^c R^d$ , worin  $R^c$  und  $R^d$  die gegebenen Definitionen besitzen, bedeuten; und  $R^7$  in der 3-Stellung und  $R^8$  in der 4-Stellung stehen.

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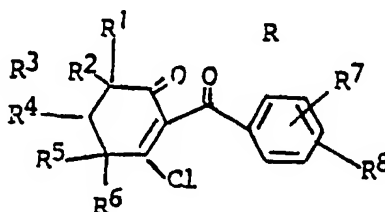
4. Verfahren zur Kontrolle unerwünschter Vegetation, dadurch gekennzeichnet, daß auf die Fläche, wo eine Kontrolle erfolgen soll, eine herbizid wirksame Menge der Verbindung nach einem der Ansprüche 1, 2 oder 3 aufgetragen wird.

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5. Herbizides Mittel, dadurch gekennzeichnet, daß es eine herbizid aktive Verbindung der Formel von 3-(substituierten Thio)-2-benzoyl-cyclohex-2-enonen nach einem der Ansprüche 1, 2 oder 3 und einen inerten Träger dafür enthält.

6. Zwischenprodukt der Strukturformel

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R Halogen,  $C_1$ - $C_2$ -Alkyl,  $C_1$ - $C_2$ -Alkoxy, Nitro; Cyano;  $C_1$ - $C_2$ -Haloalkyl oder  $R^b SO_n$  bedeutet, worin n für 0 oder 2 und  $R^b$  für  $C_1$ - $C_2$ -Alkyl stehen, bedeutet;

$R^1$  Wasserstoff oder  $C_1$ - $C_4$ -Alkyl bedeutet;

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$R^2$  Wasserstoff oder  $C_1$ - $C_4$ -Alkyl bedeutet; oder

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$R^1$  oder  $R^2$  zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen bedeuten;

$R^3$  Wasserstoff oder  $C_1$ - $C_4$ -Alkyl bedeutet;

$R^4$  Wasserstoff oder  $C_1$ - $C_4$ -Alkyl bedeutet; oder

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worin

$R^3$  und  $R^4$  zusammen Oxo bedeuten;

$R^5$  Wasserstoff oder  $C_1$ - $C_2$ -Alkyl bedeutet;

$R^6$  Wasserstoff oder  $C_1$ - $C_2$ -Alkyl bedeutet; oder

## EP 0 249 150 B1

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$R^5$  und  $R^6$  zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen bedeuten;

$R^7$  und  $R^8$ , die in den 3-, 4- und 5-Stellungen des Benzoyl-Molekülteils als Substituenten vorhanden sind, unabhängig (1) Wasserstoff; (2) Halogen; (3)  $C_1$ - $C_4$ -Alkyl; (4)  $C_1$ - $C_4$ -Alkoxy; (5) Trifluormethoxy; (6) Cyano; (7) Nitro; (8)  $C_1$ - $C_4$ -Haloalkyl; (9)  $R^bSO_n$ -, worin n für die ganze Zahl 0, 1 oder 2 steht; und  $R^b$  für (a)  $C_1$ - $C_4$ -Alkyl; (b)  $C_1$ - $C_4$ -Alkyl, substituiert mit Halogen oder Cyano; (c) Phenyl; oder (d) Benzyl steht; (10)  $-NR^cR^d$ -, worin  $R^c$  und  $R^d$  unabhängig für Wasserstoff oder  $C_1$ - $C_4$ -Alkyl stehen; (11)  $R^eC(O)$ -, worin  $R^e$  für  $C_1$ - $C_4$ -Alkyl oder  $C_1$ - $C_4$ -Alkoxy steht; (12)  $SO_2NR^cR^d$ -, worin  $R^c$  und  $R^d$  die gegebenen Definitionen besitzen; oder (13)  $-N(R^c)C(O)R^d$ -, worin  $R^c$  und  $R^d$  die gegebenen Definitionen besitzen, bedeuten.